https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

A time series analysis of transparent exopolymer particle distributions and C:N stoichiometry in the subtropical North Pacific: a key process in net community production and preformed nitrate anomalies?

Kieran Curran[1], Tracy Villareal[2], Robert T. Letscher[1,3]

1 Ocean Process Analysis Laboratory, University of New Hampshire, Durham, NH, 03824 USA
2 Marine Science Institute, University of Texas at Austin, Port Aransas, TX 78373 USA
3 Department of Earth Sciences, University of New Hampshire, Durham, NH 03824 USA

Correspondence to: Robert T. Letscher (robert.letscher@unh.edu)

Abstract

Within the oligotrophic subtropical oceans, summertime DIC drawdown despite nutrient limitation in surface waters and subsurface oxygen consumption in the absence of Redfieldian stoichiometric nitrate release are two phenomena still awaiting a full mechanistic characterization. The distribution, intensity and seasonality of these phenomena are identified with preformed nitrate as a tracer, where negative preformed nitrate (NPN) anomalies below the euphotic zone correspond to oxygen consumption without Redfieldian NO_3^- release, and positive performed nitrate (PPN) anomalies found within the upper 100m occur where O_2 is produced without stoichiometric NO_3^- drawdown. Many processes that may contribute to these anomalies including N_2 fixation, non-Redfieldian DOM cycling, vertically migrating phytoplankton, heterotrophic NO_3^- uptake and vertical NO_3^- injection events have been measured or modelled, yet generally cannot fully account for the magnitudes of preformed nitrate anomalies and excess DIC drawdown observed in many oligotrophic subtropical waters. One other candidate process that may contribute to both phenomena is the formation of carbon-rich transparent exopolymer particles (TEP) and Coomassie-stainable particles (CSP) from dissolved organic precursors in surface waters and their subsequent remineralization below the subsurface chlorophyll maximum (SCM). However, few data exist to quantify exopolymer production and vertical distributions in oligotrophic oceans over an annual cycle, which is necessary to understand their potential role in the evolution of seasonal preformed nitrate anomalies and DIC drawdown.

To investigate the significance of exopolymer formation and export to North Pacific subtropical gyre biogeochemistry, we undertook a multi-year time-series (Jan 2020 – Sep 2022) analysis of TEP, CSP and total dissolved polysaccharides concentrations at Station ALOHA (22˚45',158 ˚W), and along a transect from 22˚45' to 31˚N to measure latitudinal variability in June 2021. Exopolymer C:N stoichiometry at Station ALOHA varied between 16.4 – 34.3, with values being more carbon-rich in summer; ratios were higher (32-38) toward the gyre centre at 31˚N. TEP concentrations were consistently elevated in surface waters through Spring-Autumn (4-8 µM C after carbon conversion) at Station ALOHA with lower concentrations (~1.5-3 µM C) and more uniform vertical distribution during winter, indicating that TEP accumulated in surface waters may vertically sink and be exported with winter mixing. The accumulation of TEP in surface waters through Spring-Autumn and its subsequent export may account for 6.5-20% of net community production (NCP), helping reduce the estimated imbalance of N supply and N demand at this site to <10%. The upper ocean TEP cycle may explain 22-67% of the observed PPN/NPN anomalies, helping to close the C, N, and O_2 budgets at station ALOHA, while leaving room for significant contributions

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

from other processes such as vertically migrating phytoplankton and heterotrophic nitrate uptake to be further validated. These results suggest that exopolymer production and cycling may be more important to open ocean carbon biogeochemistry than previously expected, with considerable seasonality and spatial variability influenced by physical processes and phytoplankton activity.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

1 Introduction

Subtropical oceans constitute one of earth's largest biomes, where the euphotic water column exhibits sustained macronutrient limitation due to strong thermal stratification (Reygondeau et al., 2013). Consistently low euphotic zone chlorophyll concentrations observed in these regions lead to depressed primary production estimates using ocean-colour satellite and bio-optical float profile data (Longhurst et al., 1995; Long et al., 2021; Westberry et al., 2023), Despite this assumption of low productivity, various measured rates of annual net community production (NCP) and total annual carbon export from the ocean subtropics suggest a biological pump strength that is maintained at levels consistent with other mesotrophic oceanic regions (Gruber et al., 1998; Emerson, 2014; Teng et al., 2014; Roshan and DeVries, 2017; Quay et al., 2020; Karl et al., 2021).

Moderate rates of summertime surface dissolved inorganic carbon (DIC) drawdown are observed in low-chlorophyll Atlantic and Pacific subtropical oceans (2-3 mol C m^{-2} y^{-1}) despite limiting nitrate and phosphate concentrations, and stratification that would seem to limit diapycnal supply of nutrients to the euphotic zone for most of the year (Sambrotto et al., 1993; Michaels et al., 1994; Dave and Lozier, 2010; Williams et al., 2013; Emerson, 2014). Processes of nutrient enrichment such as N_2 fixation, episodic mixing events, and iron-rich dust deposition are unable to fully account for sufficient nutrient supply to sustain this persistent summertime anomaly (Johnson et al., 2010; Chow et al., 2017; Fawcett et al., 2018; Letscher and Villareal, 2018; Letelier et al., 2019; Karl et al., 2021). In addition, most subtropical regions exhibit respiration without concomitant nitrate release expected from the remineralization of Redfieldian organic matter, producing a widespread negative preformed nitrate ($preNO_3^-$) anomaly between ~120-180m (Emerson and Hayward, 1995; Abell et al., 2005; Ascani et al., 2013; Letscher and Villareal, 2018; Smyth and Letscher, 2023). The introduction of allochthonous macronutrient supply to the surface mixed layer (SML) or the production and export of non-Redfieldian organic matter (high elemental carbon:nitrogen ratio) within the SML are two potential processes which may couple these two phenomena and help explain the elevated surface DIC drawdown and negative $preNO_3^-$ below the sub-surface chlorophyll maximum (SCM) in these regions.

Transparent exopolymer particles (TEP), mostly comprised of acidic polysaccharides, are ubiquitous throughout the oceans, where they tend to accumulate in surface waters due to their low density (Azetsu-Scott and Passow, 2004). Exopolymers are typically observed as being carbon-rich, with C:N ratios of >20:1 (Mari et al., 2001; Engel and Passow, 2001; Passow, 2002b; Guo et al., 2022), which makes them a candidate for SML DIC drawdown with minimal nitrogen requirement, particularly if composed of pure carbohydrate (e.g. 1 C : 1 O_2 : 0 N). While most abundant during large blooms of phytoplankton in eutrophic waters, TEP and their precursors are produced by a wide variety of phytoplankton and bacteria across different marine and aquatic environments (Passow et al., 1994; Nosaka et al., 2017; Zamanillo et al., 2019). Sinking exopolymer aggregates constitute a significant flux of POC to the upper mesopelagic zone, where much of this organic matter may be consumed by aggregate-associated bacteria (Wurl et al., 2011b; Nagata et al., 2021) and sometimes zooplankton (Ling and Alldredge, 2003).

TEP production from phytoplankton exudates is associated with excess DIC drawdown even in nutrient-replete waters, with carbon overconsumption as high as 30-40% with respect to nitrate and phosphate removal and POM C:N:P stoichiometry (Toggweiler, 1993). In addition to excess DIC consumption, SML exopolymer production may increase as cells are stressed by nutrient limitation or photo-oxidative stress

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

(Berman-Frank et al., 2007; Ortega-Retuerta et al., 2009a; Iuculano et al., 2017), both conditions being persistent in many subtropical surface waters. Therefore, despite low microbial biomass in these oligotrophic regions, significant TEP production and seasonal variability may still occur.

Given that different oligotrophic regions exhibit significant variability in the elemental stoichiometry of organic matter including biomass (Martiny et al., 2013), detrital POM, and DOM (Letscher and Moore, 2015; Liang et al., 2023), across depth and time, region-specific measurements are needed to quantify the importance of exopolymer particles to pelagic biogeochemistry of different regions (McCarthy et al., 1996; Mari et al., 2001; Passow, 2002b; Beauvais et al., 2003). In this study, we aim to assess whether significant depth, temporal, and latitudinal gradients exist in exopolymer abundance and its associated C:N content that may help to explain the excess DIC drawdown/observed productivity and seasonal subsurface preNO_3^- anomalies in the subtropical oceans. Over three years we collected measurements in the North Pacific Subtropical Gyre (NPSG) of two classes of exopolymers: carbohydrate-rich transparent exopolymer particles (TEP) and protein-containing Coomassie-stainable particles (CSP) in addition to dissolved carbohydrate concentrations, which are precursor molecules of larger exopolymer particles (Passow, 2000; Ortega-Retuerta et al., 2009b; Arnosti et al., 2021), to quantify their concentrations, vertical distributions, and seasonal and latitudinal variability. In order to produce quantitative estimates of TEP and CSP concentrations we also directly estimated the organic C and N content of exopolymers spontaneously assembled under controlled conditions in the field to convert TEP and CSP values to carbon and nitrogen equivalents. With these quantitative estimates of TEP-C and CSP-N concentrations, we then discuss the significance of exopolymers and dissolved carbohydrates to overall organic carbon biogeochemistry in the study region and subtropical oceans more generally.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

2 Methods

2.1 Sample collection

Water samples for measurements of TEP, CSP, and dissolved polysaccharides were collected using a Niskin rosette onboard the RV *Kilo Moana* from 15 cruises between January 2020 and September 2022. 14 cruises were part of the Hawaiian Ocean Time-series (HOT) sampling program at Station ALOHA (22° 45' N 158° W), with 1 cruise sampling 10 stations in the North Pacific Gyre along a nominal 158ºW transect from Station ALOHA to 31° N during June 2021, also on RV *Kilo Moana* (Fig. 1). Vertical profiles of salinity (Sea-Bird SBE-09), temperature (Sea-Bird SBE-3 Plus) and oxygen (Sea-Bird SBE-43) were also collected from the rosette CTD instrument package.

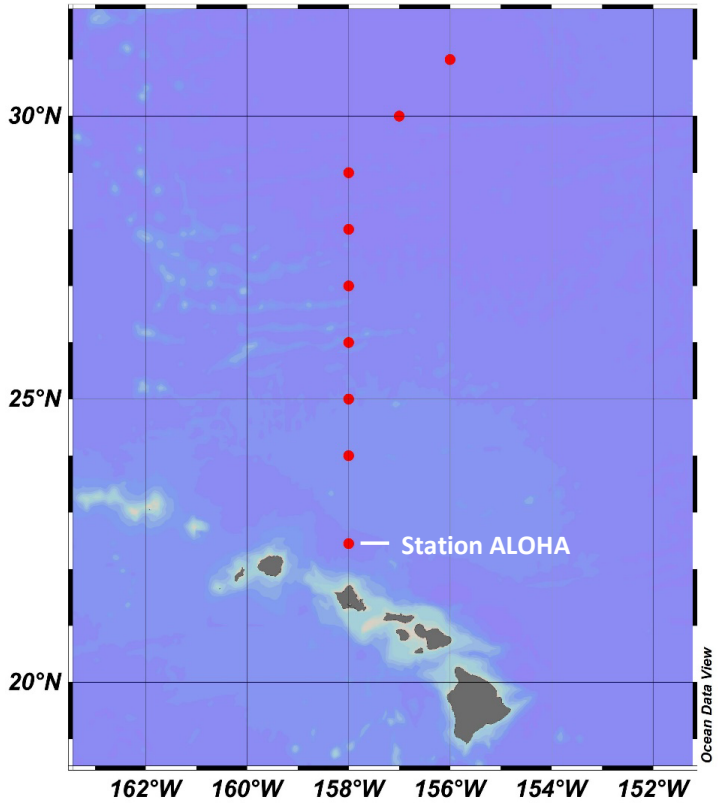


Figure 1. Map showing the location of Station ALOHA where time series measurements were collected and the stations along the June 2021 transect between ALOHA and 31°N.

2.2 Quantification of transparent exopolymer particles (TEP) and Coomassie-stainable particles (CSP)

Water samples for TEP and CSP (0.5-2.0L) were taken from 5-8 depths and stored in polycarbonate bottles (Corning) in blacked-out carriers until filtration. Samples were processed from deepest to shallowest to minimize any effects of small temperature changes on exopolymer formation dynamics. Water samples

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

for TEP and CSP were filtered using 0.4 µm pore-size, 25mm diameter polycarbonate filters (Whatman) using a peristaltic pump (Masterflex). Filters were then placed onto a vacuum filtration rig and dyed with acidified (pH 2.5) 0.02% Alcian Blue (AB) solution (Alcian Blue 8X, Sigma Aldrich) for TEP samples following Bittar et al. (2015) and 0.04% Coomassie brilliant blue (CBB) (SERVA) solution (pH 7.4) for CSP samples following Cisternas-Novoa et al. (2014). Dyed filters were placed in polypropylene vials (Falcon) and frozen at -20ºC, and 2-day shipped back to the shore-based laboratory in ice-packed coolers (Pelican). TEP samples were extracted in 6ml 80% sulphuric acid solution for 2 hrs and absorbance read at 787nm. CSP samples were extracted in 4ml 3% sodium dodecyl sulphate (SDS) in 50% isopropyl alcohol solution for 2 hrs at 37°C under ultrasonication and read at 615nm. Absorbance values were blanked against the same type of polycarbonate filters after filtration of 500ml ultrapure water. Blanks were also taken with 500ml 0.2µm filtered seawater to check that there was no bias from sub-0.2µm organic material from seawater that could be retained on the filters. These blanks were not significantly different and had a combined coefficient of variation of 0.039. Absorbance values were calibrated against a dilution series of xanthan gum (Sigma) and bovine albumin (BA) (Sigma) for TEP and CSP respectively. Concentration units are therefore expressed as µg C L^{-1} in xanthan equivalents and µg N L^{-1} in bovine albumin equivalents preceding any subsequent conversions. TEP sample replicates had a mean coefficient of variation of 0.04 and CSP samples 0.14 (n=24) from 8 sets of triplicate measurements.

2.3 Dissolved carbohydrates

Water samples for dissolved carbohydrate analysis were gravity filtered from the Niskin rosette using a 47mm combusted GF/F filter (Whatman) (0.7µm nominal pore size) into acid cleaned and furnaced glass vials. Vials were frozen at -20ºC and transported similar to above for lab analysis. Using the approach of Myklestad et al (1997), total HCl-hydrolysable carbohydrates (TCHO) were measured against a glucose calibration standard and expressed in µM carbon. The method uses the alkaline ferricyanide reaction with 2,4,6-tripyridyl-*s*-triazine (TPTZ) that produces a deep violet color with reduced iron, allowing sensitive measurement of low carbohydrate concentrations with spectrophotometry. Reagents were made fresh for each run of samples and kept in blacked-out glassware. Coefficients of variation ranged between 2.5% for low concentrations (<20 µM) to 0.9% for high concentrations (>30 µM) of carbohydrate.

2.4 Carbon and Nitrogen conversion factors

During field sampling at station ALOHA (22.75°N, 158°W) and from 31° N, 156°W in June 2021 and October 2021 from station ALOHA alone, 3 x 10 litre volumes of seawater from two depths (5m, 125m) were filtered through a 0.2 µm capsule filter (Pall) into opaque HDPE plastic bottles and stored in the dark while at sea at sample depth temperature ±1°C. Bottles were left for 80-100hrs to allow sufficient time for exopolymer to spontaneously reform from the dissolved fraction. From these bottles, duplicate filtrations (1.5L) were performed for TEP and CSP concentrations and duplicate filtrations for particulate carbon and nitrogen were taken onto 47mm GF filters (Whatman) for CHN analysis of the collected exopolymer particles.

Particulate carbon and nitrogen data were then used with the measurements of TEP and CSP to convert xanthan and bovine albumin equivalents to µM C and µM N using carbon and nitrogen conversion factors (CCF and NCF).

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

$$Carbon\ conversion\ factor = \frac{\mu M\ Particulate\ Carbon}{\mu g\ Xanthan\ equiv\ L^{-1}} \quad (1)$$

$$Nitrogen\ conversion\ factor = \frac{\mu M\ Particulate\ Nitrogen}{\mu g\ BA\ equiv\ L^{-1}} \quad (2)$$

TEP carbon (TEP-C) and CSP nitrogen (CSP-N) concentrations are thereafter converted and expressed in µM units of carbon and nitrogen respectively.

3 Results & Discussion

3.1 Carbon and Nitrogen conversion factors

Table 1. CSP-N and TEP-C conversion factors and exopolymer C:N ratios measured from exopolymer ingrowth incubations of 0.2 µm-filtered seawater conducted in June and October '21 at station ALOHA and at the northern end of the June '21 transect (31°N, 156°W); values in parentheses are coefficients of variation.

Conversions	CSP-N Jun 21	CSP-N Oct 21	TEP-C Jun 21	TEP-C Oct 21	C:N Jun 21	C:N Oct 21
ALOHA 5 m	0.018 (0.03)	0.012 (0.18)	0.529 (0.02)	0.577 (0.02)	25.7 (0.01)	18.54 (0.16)
ALOHA 125 m	0.005 (0.23)	0.013 (0.27)	0.627 (0.05)	0.600 (0.19)	34.3 (0.11)	16.40 (0.36)
31°N 5m	0.004 (0.05)		0.656 (0.12)		33.2 (0.04)	
31°N 125m	0.003 (0.19)		0.759 (0.05)		38.1 (0.01)	

Carbon conversion factors for TEP-C at station ALOHA varied between 0.529-0.627 µM C per µg xanthan equivalent L^{-1} with mean surface values being lower than at 125 m (Table 1). These values are consistent with the frequently used conversion factor of 0.6 from Engel and Passow (2001). Nitrogen conversion factors for CSP-N varied by a factor of ~6 between 0.003-0.018 with lower organic nitrogen content found at 31ºN than at station ALOHA (Table 1.). C:N ratio (16.4-34.3) at ALOHA varied more than carbon conversion factors (0.529-0.627), e.g. by a factor of ~2 and ~1.2 respectively, with summertime samples from 125 m being most carbon-rich and samples from October at 125 m having the lowest C:N ratios. All samples were carbon-rich with respect to the canonical Redfield ratio, with exopolymer C:N ratios at station ALOHA being significantly higher in summer than autumn at 5 m ($p=0.008$) and 125 m ($p=0.003$) using one-factor ANOVA, consistent with the observations of (Michaels et al., 1994). Summertime C:N ratios were higher in northern gyre-associated waters (31°N) than at station ALOHA, e.g. 33 – 38 vs. 26 – 34, however only significantly so for 5 m samples ($p<0.001$).

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

3.2 Interannual variation in TEP and CSP at station ALOHA

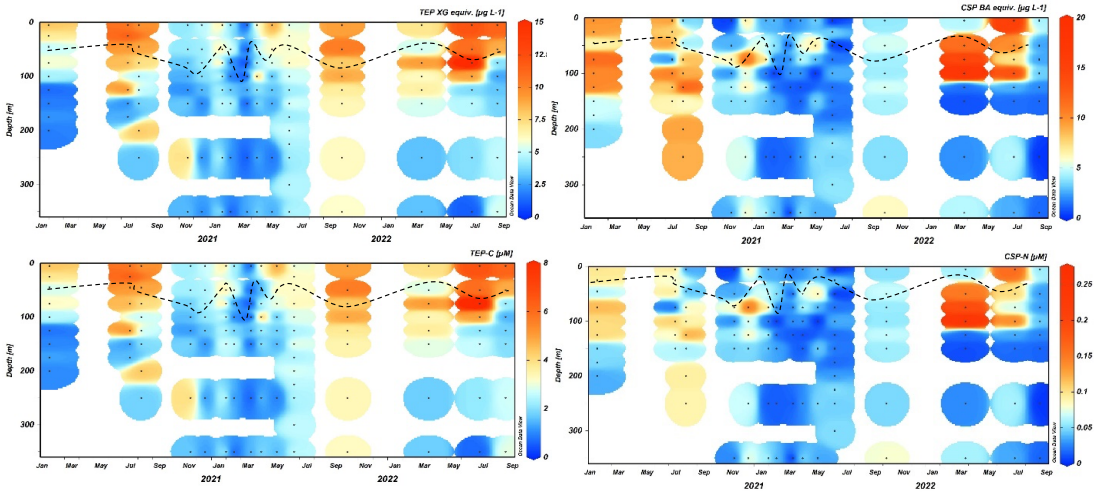


Figure 2. Time series of TEP and CSP measured in xanthan gum (XG) and bovine albumen (BA) equivalents per litre (top) and converted to µM C and µM N (bottom) at station ALOHA. Dashed line shows mixed layer depth calculated from HOT CTD data as 0.125°C decrease in temperature from the 10 m value.

At station ALOHA, TEP concentrations were highest during the summer months where values peaked in surface waters (8 – 15 XG eq L^{-1}; 4 – 8 µM C), with decreasing TEP concentrations below the SCM to underlying mesopelagic water (1 – 5 XG eq L^{-1}; 0.5 – 3 µM C; Figure 2). TEP concentrations were generally lower (2 – 7 XG eq L^{-1}; 1 – 4 µM C), with less pronounced vertical gradients during winter months, suggesting either export of accumulated TEP from surface waters or a background of non-seasonal production or abiotic formation in deeper waters. Moderate concentrations of TEP (3 – 6 XG eq L^{-1}; 2-3 µM) were observed below both the surface mixed layer and above the sub-surface chlorophyll maximum (SCM) (110-130 m) throughout most of the sampling period. Interannual variation in TEP concentrations is approximately ± 15 – 40%, with May – July 2021 having lower concentrations than similar periods in 2020 and 2022, and March 2021 exhibiting the lowest upper 100 m concentrations (coinciding with deepening of the SML to 110 m after a series of storms and heavy rainfall).

CSP distribution at station ALOHA was more variable than TEP, with less distinct vertical gradients and greater interannual variation at specific depths (Figure 2). CSP concentrations appear to be distributed differently to TEP with high concentrations (6 – 18 BA eq L^{-1}; 0.1 – 0.2 µM N) below the SML (50 – 100 m) and around the top of the SCM (100-125 m), consistent with the general distributions measured by Cisternas-Novoa et al. (2015) for the Sargasso Sea. CSP in 2021 was 2 – 8 BA eq L^{-1}; 0.01 – 0.0.07 µM N throughout the upper 300 m, similar to sub-SCM and mesopelagic (>125 m) CSP concentrations in 2020 and 2022, lacking an upper ocean seasonal peak (Fig. 2). As with TEP, CSP concentrations were observed to be greater in March 2022 than post-storms in March 2021.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

3.3 Climatologies of TEP-C and CSP-N with Particulate Carbon and Nitrogen

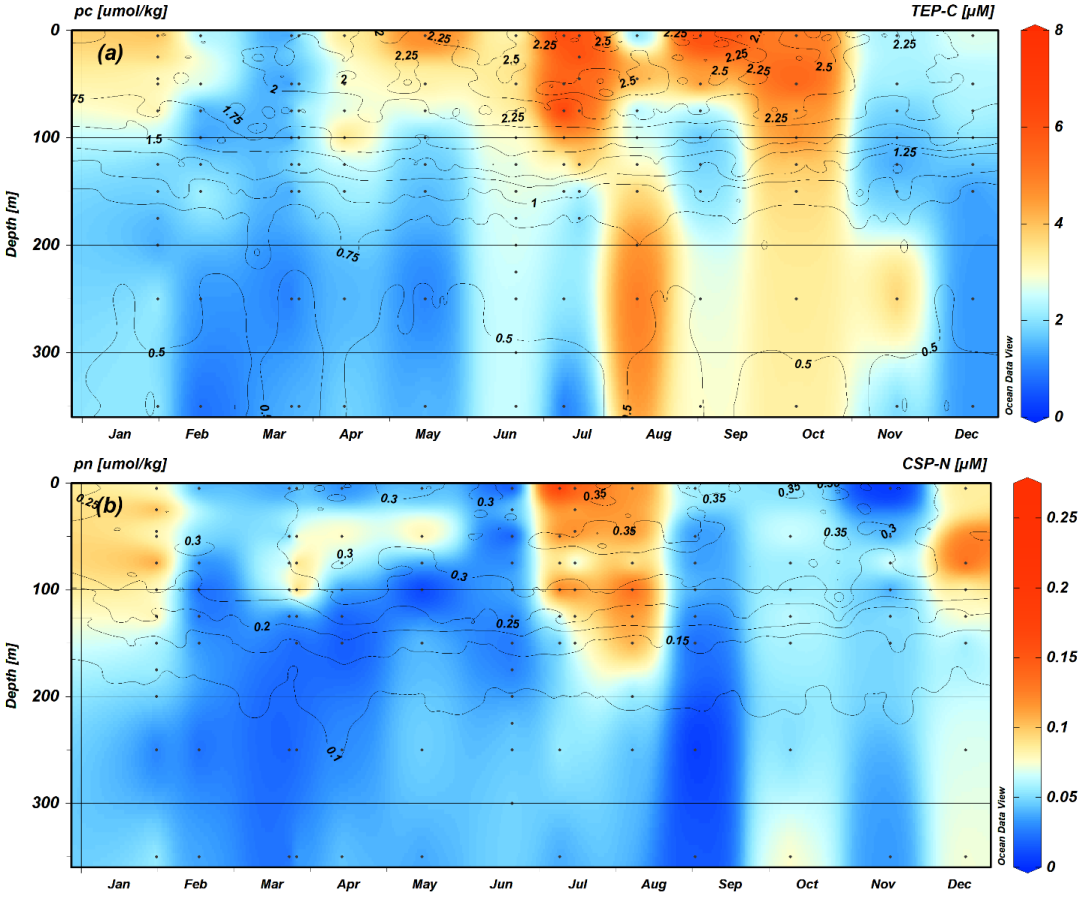


Figure 3. TEP-C (a) and CSP-N (b) (µM) concentration climatologies for 2020-2022 data measured at station ALOHA overlayed with contours from climatologies of particulate carbon (a) and particulate nitrogen (b) (µmol kg^{-1}) from the Hawaiian Ocean Time-series dataset (1989-2020 data).

TEP exhibits a seasonal pattern with elevated concentrations found in the upper 100 m beginning in April/May (3 – 4 µM) increasing to an annual maximum in late June through early October (5 – 8 µM), followed by a decrease towards an annual minimum in February/March (1 – 2 µM) (Fig. 3a). TEP concentrations below 100 m are ~1 – 2 µM from December through June, increasing to 2 – 4 µM from June through November, concurrent with the seasonal maxima in upper 100 m TEP. These moderate concentrations of TEP below 100 m present during summer/autumn may be due to sinking aggregates as TEP accumulate through spring-summer and form aggregates before sinking, consistent with the contemporaneous peak in particulate export rates of ~30-55 mg C m^{-2} d^{-1} at station ALOHA (Emerson et al., 1997; Karl et al., 2012; Böttjer et al., 2017; Karl et al., 2021). The CSP climatology suggests two seasonal concentration maxima in the upper 100 – 130 m occurring in July/August and in December/January (0.07 – 0.13 µM) (Fig. 3b). CSP concentrations in other months and below these depths are <0.06 µM. Comparing TEP and CSP concentrations to climatologies of particulate carbon (PC) and nitrogen (PN)

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

respectively at station ALOHA (1989-2020) it is apparent that measured TEP concentrations reflect variation in euphotic PC more closely that CSP does PN, particularly for samples taken May-October. Elevated CSP-N concentrations during summer months (0.12-0.24 µM N) correspond with PN maxima, but during winter and spring CSP-N comprises a smaller proportion of PN. While CSP-N values are lower in magnitude to PN concentrations, TEP-C is frequently observed to exceed background PC concentration at station ALOHA, which may be an artifact of filtrations for PC and PN analysis losing exopolymers during GF/F filtration or excess dye binding to particles using the colorimetric method of measuring TEP and CSP (Passow, 2002b; Bar-Zeev et al., 2011; Annane et al., 2015; Ortega-Retuerta et al., 2019; Nagata et al., 2021). The difference in nominal pore size between GF/F filters used to sample PC (0.7 µm) and the 0.4 µm pore-size polycarbonate filters used for TEP may also lead to sampling errors when comparing TEP-C and PC/POC, as most of these particles are small (<3 µm diameter) particularly in the upper 200 m, with particles tending larger as they age or sink and aggregate through the mesopelagic (Engel et al., 2020). It is therefore likely that TEP-C to PC ratios are inconsistent with depth and more accurate for samples containing larger particles. Strands of microgels and larger particles may be easily pulled through GF/F filters under vacuum pressure and may be disaggregated when sampled in standard sediment catching methodology due to turbulence, break up at saline density layer, solubilization or rapid remineralization or preferential consumption by swimmers (Smith et al., 1992; Buesseler et al., 2007; Fawcett et al., 2018).

In addition to the variable size spectrum of TEP particles, the electrochemistry that allows the aggregation of polymers into micro and macroscopic gels (principally divalent cations Ca^{2+} and Mg^{2+}) may be affected during filtration, and to a different degree with various polycarbonate and GF/F filters (Chin et al., 1998; Meers et al., 2006). If this is the case, then gels >0.4 µm that would otherwise be retained may be broken apart into constituent polymers or smaller nanogels that can pass through the filter. This would lead to TEP being quantified in the DOM fraction and lead to an overestimate of dissolved to particulate fractions of organic matter.

3.4 Patterns of TEP and CSP with respect to particulate C and N at station ALOHA

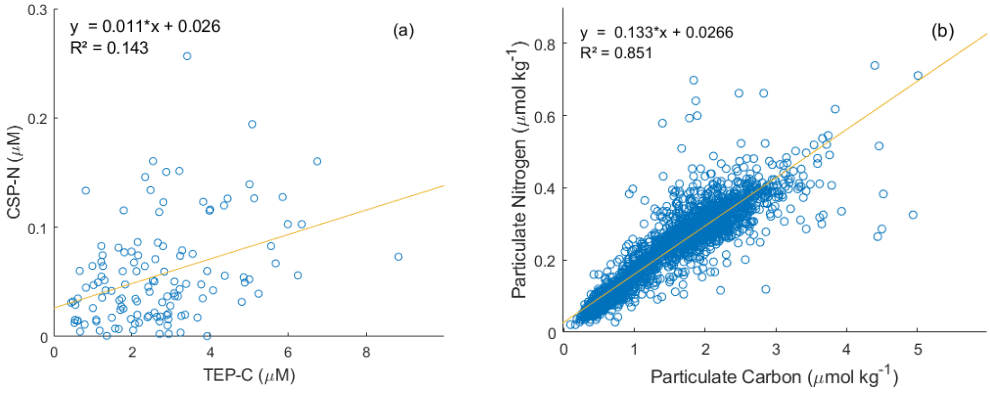


Figure 4. Measured CSP-N and TEP-C concentrations within the upper 350 m at station ALOHA from this study (a) and model II linear regression of particulate nitrogen to particulate carbon from the HOT dataset (1989-2020 data).

Measured PC and PN (Fig. 4) concentrations are well correlated at station ALOHA and the mean C:N ratio computed from the inverse of the slope (7.55) is slightly higher than the canonical Redfield ratio (6.63),

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

with some deviation at high particulate carbon concentrations and slight relative N-enrichment for most samples from the SCM. In contrast, TEP-C and CSP-N concentrations show very weak correlation or trends at specific sampling depths despite having some periods of similar seasonality and depth distributions through the 2020-2022 sampling period (e.g. elevated upper ocean TEP and CSP during July/August (Fig. 2, 3). The weak correlation of TEP-C with CSP-N concentration suggests different formation, consumption, and/or export dynamics for each group of exopolymers.

3.5 TEP and rates of primary production

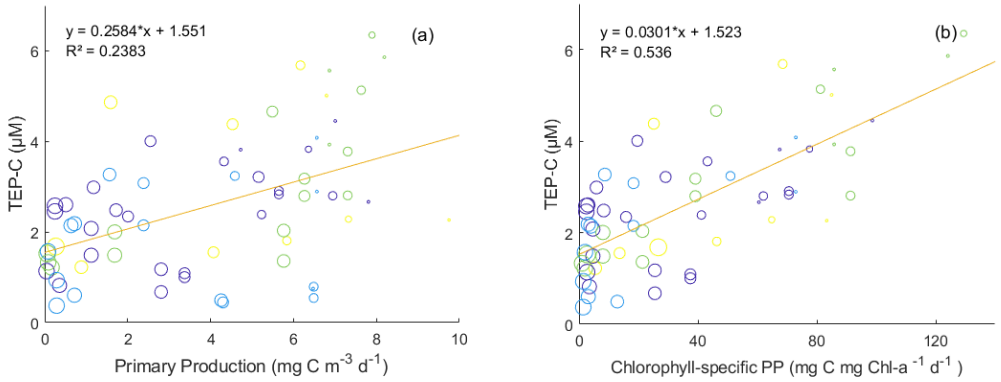


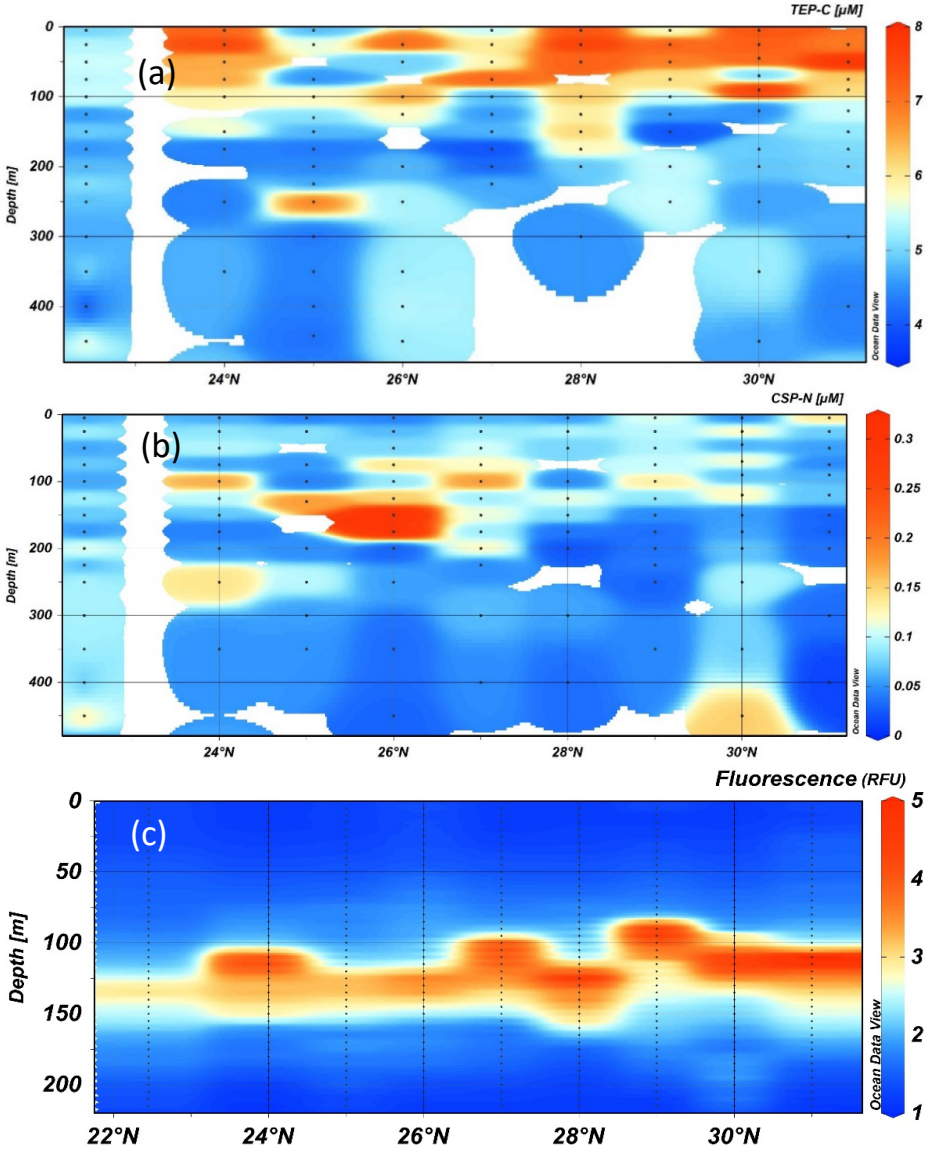
Figure 5. Model II linear regression of TEP-C from this study against same-depth daily primary production (a) and chlorophyll-specific primary production (b) measured at station ALOHA. Circle size indicates depth: larger circles are deeper samples. Colour denotes season: Purple = winter, Blue = Spring, Green = Summer, Yellow = Autumn

As TEP production, abiotic formation, and consumption / degradation dynamics are often attributed to phytoplankton community structure and downwelling irradiance intensity (Zamanillo et al., 2019; Bar-Zeev et al., 2011; Ortega-Retuerta et al., 2009a; Berman-Frank et al., 2007; Passow, 2002a), daily primary production (PP) measurements taken during HOT cruises were compared with TEP concentrations, indicating a weak positive correlation for overall PP and a stronger correlation for chlorophyll-normalized PP (Fig. 5). The co-occurrence of higher TEP-C concentrations and high chlorophyll-specific primary production values in surface waters despite nutrient limitation may be indicative of enhanced release of TEP carbohydrate precursors in addition to downregulation of photosynthetic pigment synthesis in light-saturated surface waters (Rabouille et al., 2017; Thompson et al., 2018). The highest values of primary productivity and TEP concentration (>4 µM) were observed in Summer and Fall samples. There are too few data to determine whether TEP-C to PP ratios vary with season. CSP-N showed no such correlation with primary production within this dataset. Although these results may be expected simply from the vertical gradients observed in TEP at station ALOHA and across the June ’21 transect, chlorophyll-normalized PP gives some information on whether TEP concentrations are only associated with surface accumulation or formation around peak microbial biomass around the SCM. While this small dataset of TEP and PP matchups may indicate TEP production is occurring around the SCM owing to moderate chlorophyll-normalized PP and TEP concentrations at these depths, there are too few data at present to draw firm conclusions, particularly for near-surface water. Wurl et al. (2011) found a similar disconnect between microbial activity and exopolymer distributions: variations in measured TEP production rates

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

across different Pacific waters (including late-summer samples from station ALOHA) were not associated with phytoplankton blooms, changes in chlorophyll concentrations or fluorescence, with abiotic formation of TEP easily maintaining observed concentrations in the surface mixed layer (8-12 µM C L^{-1} d^{-1}).

3.6 TEP and CSP concentrations on June '21 transect 22.75°N to 31°N



https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

Figure 6. TEP-C (a), CSP-N (b) concentrations and CTD-mounted fluorescence (c) measured during the June 2021 transect from 22.75°N to 31°N along ~158ºW.

Transects of TEP-C and CSP-N in the upper 450 m taken between 22.75°N and 31°N along ~158ºW (Fig. 6) during June 2021 show an increase in surface TEP concentrations towards the gyre centre, with two occupations of station ALOHA at the beginning and end of the transect, separated by ten days having the lowest integrated TEP concentrations and degree of vertical gradient. From 24-31°N all stations exhibited pronounced vertical gradients in TEP concentrations between the surface and below the SCM on the order of ~2-3 µM TEP-C. At stations 24ºN and 28°N, moderate TEP-C concentrations (5.5 – 7 µM) extended into the SCM whereas high concentrations (6 – 8 µM) were restricted to the upper 75 m at 29°N and 31°N. It is unclear whether this difference is attributable to the production of buoyant TEP in the SCM, varying depths of TEP consumers, surface turbulence from wind forcing, transient variations such as phytoplankton nutrient or oxidative stress, or photoacclimation responses and concomitant exudate production between sites (Sun et al., 2018; Prairie et al., 2019). It is also of note that most stations exhibited a local increase in TEP-C at ~10-20 m immediately above the top of the SCM. The surface maxima in TEP-C present at 28-31ºN was ~8 µM (Fig. 6a), similar in magnitude to the surface maxima accumulating seasonally in the station ALOHA time-series (Fig. 2; 3a). However, the vertical TEP-C gradients encountered from 24-31ºN in June 2021 were ~2-3 µM, approximately half that observed seasonally at station ALOHA (Fig. 2). The observed ~2 µM latitudinal gradient in 0-100 m TEP-C concentration may also be attributed to the build-up of less labile or less export-prone (or coagulation efficient) TEP as waters move towards the gyre interior (Mari et al., 2007; Rochelle-Newall et al., 2010; Mari et al., 2017), a feature that is also observed for the marine DOC pool (Hansell et al., 2009).

Distributions of CSP-N throughout the transect did not correspond to those of TEP-C (Fig. 6). CSP-N concentrations were highest (0.15-0.26 µM) between 75-200 m for stations 24-29°N. Profiles at 22.75°N, 30ºN and 31°N were more uniform with moderate CSP-N concentrations (0.05 – 0.12 µM) observed below 250 m. CSP appears to be more closely associated with peak fluorescence signals (Fig. 6c) while TEP is most abundant in the surface. This disconnect between TEP and CSP distributions suggests different dynamics in formation, residence time and decomposition and export process between the two classes of exopolymers (Grossart et al., 2006; Engel et al., 2015; Thornton, 2018).

Previous observations of TEP and CSP particle concentrations in high latitude oceans and temperate shelf seas have observed that both exopolymers are coupled to chlorophyll distributions (Beauvais et al., 2003; Busch et al., 2017; Nosaka et al., 2017; Anastasi, n.d.; von Jackowski et al., 2020). Other mid-latitude regions such as the Sargasso Sea (Cisternas-Novoa et al., 2015) and Catalan Sea (Zamanillo et al., 2021) exhibit different dynamics, where TEP is disconnected from CSP distributions as was observed in this study in the subtropical North Pacific.

The seasonal, interannual and latitudinal variation of TEP and CSP observed in this study reinforces the building evidence that exopolymer production, accumulation and remineralization are not static processes, even in oligotrophic regions (Radić et al., 2006; Cisternas-Novoa et al., 2015; Engel et al., 2015; Zäncker et al., 2017). Further process experiments that incorporate TEP and CSP dynamics with respect to other biological and chemical parameters are needed to understand the biogeochemistry of each exopolymer type for a given location and season, aiding efforts to model both with respect to other parameters through depth and time at a synoptic scale.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

In addition to observations and estimates of water-column exopolymer distributions and cycling, the importance of the sea-surface microlayer to regional TEP and CSP dynamics and seasonal variations is worthy of consideration in this oligotrophic region, where surfactants are significantly enriched from underlying surface waters despite low surface PP (Wurl et al., 2011a). Surface microlayer CSP enrichment factors are often higher than for TEP (Aller et al., 2017; Zäncker et al., 2017), such that any subsequent bias in the surface mixed layer exopolymer budget may be inconsistent for TEP and CSP. Loss factors associated with aerosolization and photooxidation of exopolymers from the enriched surface microlayer are another consideration in quantifying the fate of exopolymers and thus fluxes of organic carbon from non-photosynthetic DIC uptake (Aller et al., 2017; van Pinxteren et al., 2022).

3.7 Dissolved carbohydrates

Measured concentrations of total dissolved carbohydrates (TCHO) varied between ~2.5-13 µM carbon equivalents across the June 2021 transect. TCHO distributions did show some overlap with elevated surface TEP concentrations but were not consistent with TEP concentrations below the surface mixed layer (Fig. 7b). At many stations, [TCHO] were elevated (9-12.5 µM) around and below the SCM, where [TEP-C] was low (4.5-5.5 µM).

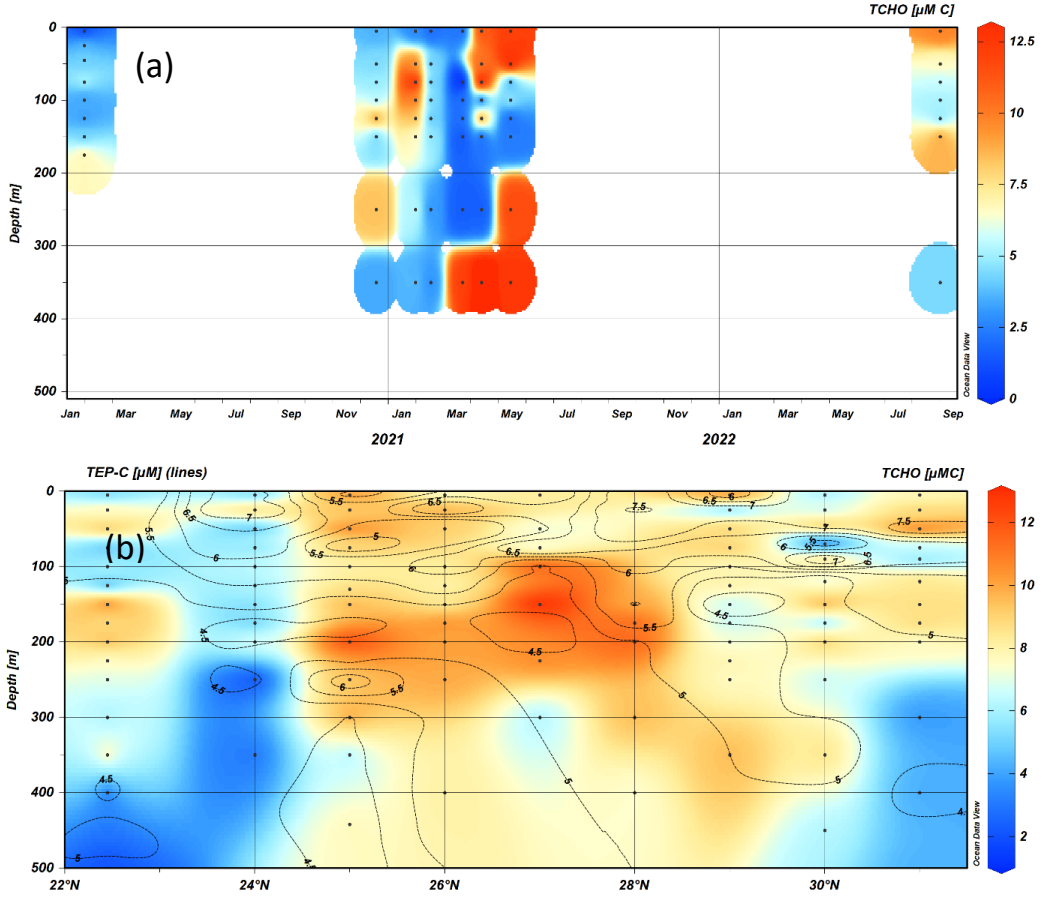


Figure 7. Reduced time series of total dissolved carbohydrates (TCHO) (µM C) at station ALOHA 2020-2021 (a).

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

Transect of TCHO concentrations during the June 2021 transect from 22.75°N to 31°N overlayed with contours of TEP-C for comparison (b).

Most stations exhibited vertical gradients between surface or SCM maxima (≥10 µM) and reduced [TCHO] (2 – 8 µM) below 250 m, but some stations were more consistent with depth (24°N, 29°N) with peak values near the surface. These patterns are generally dissimilar to TEP distributions that are elevated in surface waters.

Carbohydrate samples were taken on fewer HOT cruises than TEP and CSP samples during 2020-2022, with the only summer data being from the transect cruise. There is a marked difference in the concentrations and distribution of TCHO between winter samples in 2020 and 2021 where surface concentrations were low (2 – 6 µM) and data from spring, where concentrations are consistently high at 350 m and in the upper 50 m from April (> 10 µM). Compared to DOC measurements taken at station ALOHA, this spring maximum at 350 m seems erroneous, but falls within the intra-annual variability of DOC at 350 m at ALOHA (± 6 µM C) and monthly variation in particulate export (Karl et al., 2021). It may be possible that some hydrolysable particulate polysaccharides are drawn through combusted GF/F filters (Nagata et al., 2021). Another potential explanation is the degradation and/or solubilization of exopolymers below the SCM where polysaccharide-specific enzyme activity is elevated (Reintjes et al., 2020).

Measurements from this study were on the lower end of marine dissolved carbohydrate measurements, but consistent with previous measurements taken within the subtropical North Pacific (Pakulski and Benner, 1994), 30-60% lower than observed across the subtropical Atlantic (Burney et al., 1979; Goldberg et al., 2010) and 40-100% higher than in the Bay of Bengal and Arabian Sea (Bhosle et al., 1998).

The observed disconnect between TEP and TCHO distributions may be attributed to both formation and degradation processes: precursors being created around the SCM by phytoplankton and resultant low-density TEP particles concentrating in surface waters or sinking TEP being hydrolyzed below the SCM by bacteria, yielding reduced TCHO concentrations. The latter process is consistent with the hypothesized remineralization of low-N organic matter requiring heterotrophic nitrate uptake, generating a negative preNO_3^- anomaly (Fawcett et al., 2018), but would require compositional analysis of TEP particles, dissolved sugars, and stable isotopic measurements of the relevant nutrient and organic matter N contents through the upper 400 m to confirm. Lastly, a lack of spatiotemporal coherence in the distributions of TEP and its precursor TCHO may result from differing timescales over which they are biotically cycled, with the latter possibly processed 3-10 times faster than other common labile organic materials like amino acids by bacteria in open ocean environments (Kaiser and Benner, 2012), enabled by a complex suite of bacterial enzymes for hydrolyzing polysaccharides and transporting carbohydrates into cells' periplasm (Reintjes et al., 2020).

3.8 Contribution of TEP production to net community production and PreNO_3^- anomalies

Here we use the seasonal study of TEP distributions from the upper 350 m at station ALOHA to quantify its potential contribution to help explain the dual enigmas of significant net community production from the mixed layer in the absence of large vertical nutrient inputs and the generation of PreNO_3^- anomalies within and immediately below the euphotic zone of the subtropical North Pacific. The potential contribution of TEP to surface excess DIC drawdown and sub-SCM negative preformed nitrate anomalies under nutrient limitation has been identified through field and lab observations, and modelling efforts (Mari et al., 2017; Fawcett et al., 2018; Letscher and Villareal, 2018; Nagata et al., 2021). The ~4-6 µM

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

TEP-C concentration gradient observed between Apr-Oct in the upper 100 m in this study, representative of the euphotic zone above the SCM at station ALOHA, and the ~100 – 300 m layer representative of the SCM and the upper mesopelagic, may account for a significant contribution of TEP to both the seasonal mixed layer dissolved inorganic carbon drawdown (NCP) and upper ocean preNO_3^- anomalies through the processes of TEP production, sinking or matter exported during winter mixing, and subsequent remineralization at depth. TEP may have a significant role in exporting low-N organic matter to underlying waters, particularly during the summer to early autumn months (Fig. 3) when the seasonal maximum in upper 100 m TEP concentrations extends vertically into the 100 – 300 m layer, suggestive of vertical sinking.

The 4-6 µM vertical TEP gradient that arises seasonally reported here , e.g. 5-8 µM in the upper 100 m Apr-Oct decreasing to 1-2 µM below, is higher than those observed by Cisternas-Novoa et al (2015) (~10 µg XG eq. L−1 / ~0.5 µM TEP-C) in the Sargasso Sea and Wurl et al. (2011) (1.4-3.2 µM TEP-C with one high-TEP station with a gradient of 27 µM TEP-C) in the subtropical North Pacific when applying the carbon-converted units measured in this study. The wintertime erasure in vertical TEP gradients between the surface and 200 m is observed in Feb-Mar and Nov-Dec samples from station ALOHA in this study (Fig. 3a), supporting the hypothesis of TEP-C export to depth of ~100 m at ALOHA and possibly deeper at latitudes further north in the subtropical North Pacific that may facilitate seasonal TEP export (beyond sinking aggregates which may occur year-round). As carbon conversion factors for TEP at station ALOHA are consistent for summer and autumn, it seems that exported TEP from the SML to depths below may be assumed to have consistent carbon content, whether it is sinking at any time of the year or exported during winter mixing, contributing to positive and negative preNO_3^- anomalies at consistent C:O_2 stoichiometry. However, the C:N ratio of TEP and CSP does appear to vary from highly carbon rich in summer, to less carbon rich in autumn, meaning respiration associated with sinking exopolymers may have variable O_2 drawdown to nitrate release throughout the year.

The background particulate carbon flux at 150 m measured at station ALOHA of 27.8 ± 9.7 mg C m^2 d^{-1} (845 ± 295 mmol C m^{-2} yr^{-1}; Karl et al. 2021) would seem to indicate that the export of even a portion of the 0-150 m integrated 750 ± 150 mmol C m^{-2} summer/fall TEP stock by either TEP sinking or vertical export following winter mixing would be a significant flux of carbon on an annual scale. Furthermore, sediment trap data indicate that particulate matter exported at station ALOHA is typically slightly above Redfieldian C:N proportions, e.g. ~8.0 (Hannides et al., 2009), while TEP measured in this study varied between 16.4 in October to 34.3 in June (Table 1). The annual NCP rate estimated from the seasonal DIC cycle within the mixed layer (~50 m) at Station ALOHA is 2.3 ± 0.8 mol m^{-2} y^{-1} (Keeling et al., 2004), thus the annual production of a surface accumulated excess TEP-C stock of 0.2-0.3 mol m^{-2} in the upper 50 m (ΔTEP = 4 – 6 µM x 50 m) may contribute 6.5-20% of the overall NCP estimated from DIC drawdown (1.5-3.1 mol m^{-2} y^{-1}).

From the calculation above, TEP production within and subsequent export below the surface mixed layer may explain up to 20% of the total NCP, but how does this estimate compare to the estimates of 'excess' DIC drawdown, that is DIC drawdown in excess of known N inputs, at this site? For this calculation, it is helpful to compute the N demand required to produce the observed NCP rate, partitioned amongst the relative proportions of POM, DOM, and TEP production. Johnson et al. (2010) computed a total N demand of 287 mmol N m^{-2} y^{-1} at station ALOHA assuming total organic matter production followed a C:N stoichiometry of 8.0, matching the sinking POM stoichiometry. Letscher & Villareal (2018) empirically determined the fraction of NCP partitioned to DOM at station ALOHA from tracer budgets in upper

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

mesopelagic isopycnal layers from the station ALOHA climatology, finding that ~50% of NCP is exported as DOM. We have computed the mean DOM C:N stoichiometry in the upper 200 m at 15.5 ± 1.3 from the same climatology. Assuming NCP is partitioned 50/50% between POM and DOM with C:N stoichiometries of 8.0 and 15.5 respectively, we compute a revised N demand of 218 mmol N m^{-2} y^{-1} to satisfy the observed 2.3 mol C m^{-2} y^{-1} NCP within the mixed layer. Johnson et al. (2010) summarized total N supply to the mixed layer at station ALOHA finding a magnitude of 144 – 201 mmol N m^{-2} y^{-1}. Thus approximately 8 – 34% (mean = 21%) of the observed NCP N requirement is not accounted for by the known N supply for the scenario where only POM and DOM production contribute to NCP. Our estimate of TEP production and its contribution to NCP at this site is 6.5 – 20%, with an observationally determined C:N stoichiometry of 16.4 – 34.3 (Table 1). Addition of TEP into the mixed layer NCP budget yields an N demand to explain TEP production of 4 – 28 mmol N m^{-2} y^{-1}, which reduces the total N demand to 174 – 208 mmol N m^{-2} y^{-1}. Comparing this N demand to the prior calculated N demand that included POM and DOM but ignored TEP, TEP contributions to the upper ocean NCP budget help explain ~57% of the unexplained 'excess DIC drawdown' from the mixed layer, reducing the overall unexplained drawdown from a mean of ~21% to ~9%.

Table 2. Estimates of the nitrogen demand partitioned amongst POM, DOM, and TEP required to satisfy each fractional contribution (^{f}NCP) of the mixed layer 2.3 mol m^{-2} y^{-1} NCP at station ALOHA using their respective C:N stoichiometries. Total N supply is taken from Johnson et al. (2010) and includes vertical NO_3 fluxes plus N_2 fixation. $^{f}NCP_{POM}$ varies as the particulate fraction not attributable to TEP or DOM ($^{f}NCP_{POM} = 1-(^{f}NCP_{TEP} + ^{f}NCP_{DOM})$), POM C:N from Hannides et al. (2009), $^{f}NCP_{DOM}$ from Letscher and Villareal (2018), DOM C:N from the upper 200 m average of the station ALOHA climatology, $^{f}NCP_{TEP}$ and TEP C:N (Table 1) from this study.

Depth integration		^{f}NCP	C:N	N demand (mmol N m^{-2} yr^{-1})	% of N demand
50m	POM	0.30-0.435	8	86-125	36-52
	DOM	0.5	15.5	74	31
	TEP	0.065-0.20	16.4-34.3	4-28	2-12
	Total demand			**174-208**	
	Total supply			**144-201**	

Lastly, we compare the seasonal TEP cycle observed at station ALOHA from 2020-2022 to previous estimates of the formation rates of residual $PreNO_3^-$ anomalies within and immediately below the euphotic zone. Letscher and Villareal (2018) estimated the seasonal (~Apr-Oct) development of a residual positive $PreNO_3^-$ (rPPN) anomaly (i.e. the residual anomaly after accounting for non-Redfield POM and DOM stoichiometry) within the upper 100 m with a climatological magnitude of 0.53 ± 0.27 µM. A similar seasonal negative $PreNO_3^-$ (rNPN) anomaly develops between ~100-150 m with a climatological magnitude of -0.54 ± 0.25 µM over a ~180-day period from Apr-Oct, consistent with surface TEP accumulation before winter mixing (Fig. 2). With assumed 1:1 C to O_2 stoichiometry of TEP formation and remineralization (as for nearly pure carbohydrate material), the consumption of 4-6 µM TEP C (at a C:N ratio of 25 ± 8) should release the equivalent of 0.12-0.35 µM NO_3 which is 23-67% of the 0.53 µM rNPN and 22-64% of the 0.54 µM rPPN mean anomalies. These values for TEP's potential contribution to rNPN assume the export of surface TEP to underlying waters 100-200 m where they are efficiently remineralized. If a large proportion of seasonal TEP production is quickly exported to the deeper

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

mesopelagic through aggregation and gravitational settling or winter mixing, then these values will likely be overestimates. Remaining mechanisms to explain the remainder of rPPN/rNPN anomaly formation include mining of sub-euphotic zone nitrate by vertically migrating phytoplankton (Pilskaln et al., 2005; Villareal et al., 2014) and heterotrophic bacterial uptake of nitrate when consuming C-rich organic matter such as TEP (Fawcett et al., 2018).

Finally, we note that moderate concentrations of TEP at 250 and 350 m (2-3 µM C) are present throughout the year at station ALOHA, but whether these concentrations represent matter exported from the surface or SCM below the depth of the rNPN anomaly (~100 – 175 m; Letscher & Villareal, 2018), or separate activity in the upper mesopelagic is unclear. Compositional analysis of TEP molecules and polysaccharide-associated enzymes throughout the water column and over an annual cycle may elucidate sources and sinks of TEP beyond physical sinking and mixing processes.

4 Conclusions

Exopolymers measured in the subtropical North Pacific were found to have seasonal and latitudinal variability, with elevated concentrations in surface waters for TEP and around the SCM for CSP. The seasonality and vertical distributions of TEP and CSP were not correlated, suggesting different production and loss processes in this region. While TEP concentrations were low compared to other regions, their highly carbon-enriched stoichiometry (particularly in summer with C:N = 26-38) means that these particles are a significant component of the euphotic POC pool. A summertime transect from 22.75° to 31°N in the North Central Pacific indicated that TEP concentrations increased towards the gyre interior, though without additional data on TEP molecular composition it is difficult to ascertain whether this is accumulation of more refractory TEP, or enhanced production/depressed export in these waters. The seasonal and latitudinal variation we observed in carbon and nitrogen conversion factors suggest using a single factor will bias many estimates of TEP-C and CSP-N from dye-binding assays. We therefore hope that more effort will be made in future studies to constrain TEP and CSP elemental stoichiometry to compare exopolymer concentrations from different depths, seasons and locations with greater confidence. TEP concentrations measured with the Alcian blue spectrophotometric method and converted to µM C with our empirically derived CCF were found to be greater than GF/F collected particulate carbon measurements. Additionally, the estimated C:N stoichiometry of 16.4 – 38.1 for TEP from this study is significantly C-rich/N-poor relative to the C:N of the sinking flux collected in sediment traps at station ALOHA, 8.0 (Hannides et al., 2009). This supports the hypotheses that TEP and marine microgels may be 'missed' by traditional sampling techniques for sinking and suspended particulate organic carbon, possibly due to disaggregation of the gel-particles upon encountering the GF/F filter or collection brine of sediment traps as well as potential rapid microbial remineralization within trap cups (Fawcett et al., 2018 and references therein). Future research is required to resolve the mechanisms leading to inefficient collection of TEP within standard marine particle sampling protocols and fully integrate TEP and marine gels sampling within marine carbon biogeochemistry studies.

Measurements of dissolved carbohydrates, the precursors to TEP formation, exhibited less consistent spatiotemporal trends and were generally not corelated with TEP with concentrations being elevated around and below the SCM during the summertime transect for some stations, but concentrated in surface waters at others. There are too few data available from our time series to assess annual variations confidently. Although only measured in low concentrations (2.5-13 µM) vs total DOC pools at station ALOHA (55-75 µM), the presence of this labile substrate below the SCM means compositional analysis of

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

these carbohydrates and exported TEP may elucidate the importance of TEP remineralization to this pool of DOM and the oxygen demand TEP and TCHO cycling requires.

The dataset presented here marks a contribution to quantifying the role of exopolymers to euphotic and upper mesopelagic biogeochemistry in the subtropical North Pacific that can be expanded on with complimentary measurements and analyses of composition, carbon budgets and formation, export and cycling rates. Work that helps to validate the sources and sinks of exopolymers within the water column is particularly important in quantifying how much carbon is exported from or cycled within surface waters (including the surface microlayer) and where these molecules are remineralized. Compositional analysis of TEP particle and dissolved carbohydrates compositions and associated proteomic or transcriptomic analyses may elucidate the vertical distribution of TEP production, enzymatic hydrolyzation and remineralization of the resulting labile monomeric sugars.

Following the conversion of semi-quantitative measurements of exopolymers from dye-binding assays, our elemental conversions to C and N units allow us to estimate the magnitude of TEP's importance to surface ocean carbon dynamics on an annual cycle. We estimate that TEP accumulation within the ~50 m mixed layer may constitute 6.5-20% (0.2-0.3 mol m^{-2} y^{-1}) of the NCP (2.3 ± 0.8 mol m^{-2} y^{-1}) at station ALOHA. With its low N requirement, TEP reduces the overall N demand needed to explain the observed NCP at this site, bringing the measured N supply and demand into near balance. If TEP is sufficiently exported below the euphotic zone by a combination of sinking and/or winter vertical mixing, its cycling can reduce the unexplained 'excess' DIC drawdown from the mixed layer by ~60%, bringing the overall unexplained excess (or missing N supply) to ~9%.

Though TEP sinking rates, remineralization rates and C:O_2 respiration stoichiometry are not addressed in this dataset, previous studies in analogous regions indicate that the summertime production of highly non-Redfieldian exopolymers and potential winter export observed in this time series may explain a significant portion of subtropical positive and negative PreNO_3^- anomalies (22-67%), consistent with this mechanism's description and modelling by Letscher and Villareal (2018). Uncertainty in the contribution of TEP to PreNO_3^- anomalies (and excess DIC drawdown) primarily results from variability in the total TEP upper ocean accumulation and its C:N ratio; with some evidence for seasonal, vertical, and latitudinal differences in these ratios evidenced in this study (Table 1). More frequent measurements of TEP concentrations and its stoichiometry from the subtropical North Pacific and elsewhere would help quantify the magnitude and causes of this variability.

Author contributions

RTL and TV conceptualized this study as part of NSF grants 1923687 and 1923667 "Transparent exopolymer and phytoplankton vertical migration as sources for preformed nitrate anomalies in the subtropical N. Pacific Ocean". KC, RTL, and HOT technicians performed fieldwork; KC performed laboratory analyses for TEP, CSP and TCHO and respective data analyses. KC, RTL, and TV contributed to writing and editing. Data from the Hawaiian Ocean Time series were obtained via the Hawaii Ocean Time-

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

series HOT-DOGS application; University of Hawai'i at Mānoa. National Science Foundation Award # 1756517.

Acknowledgements

We would like to thank the crew and technicians aboard RV Kilo Moana for their assistance in collecting samples through the COVID pandemic and assisting during the June '21 transect cruise. We are grateful to Angelicque White (UH-Manoa) for her assistance and leadership in accommodating the TEP, CSP, and TCHO sampling on the 2020-2022 HOT cruises and to Brandon Brenes (UH-Manoa) for much of the sample collection at sea. We also wish to thank former UNH graduate students Jessica Gray and Sarah Benson for their assistance with sampling during the 2021 cruise.

Financial support

This study was funded as part of NSF grant 1923687 to RTL and 1923667 to TV entitled: "Collaborative research: Transparent exopolymer and phytoplankton vertical migration as sources for preformed nitrate anomalies in the subtropical N. Pacific Ocean."

Data availability

The data reported in this study are available at: https://www.bco-dmo.org/project/772658.

Competing interests

We declare no competing interests in the undertaking and publication of this study.

References

Abell, J., Emerson, S., and Keil, R. G.: Using preformed nitrate to infer decadal changes in DOM remineralization in the subtropical North Pacific, Glob. Biogeochem. Cycles, 19, https://doi.org/10.1029/2004GB002285, 2005.

Aller, J. Y., Radway, J. C., Kilthau, W. P., Bothe, D. W., Wilson, T. W., Vaillancourt, R. D., Quinn, P. K., Coffman, D. J., Murray, B. J., and Knopf, D. A.: Size-resolved characterization of the polysaccharidic and proteinaceous components of sea spray aerosol, Atmos. Environ., 154, 331–347, https://doi.org/10.1016/j.atmosenv.2017.01.053, 2017.

Anastasi, G.: OBSERVATIONS AND MODELLING OF TRANSPARENT EXOPOLYMER PARTICLES (TEP) AND THEIR ROLE IN CARBON CYCLING IN SHELF SEAS, 237, n.d.

Annane, S., St-Amand, L., Starr, M., Pelletier, E., and Ferreyra, G. A.: Contribution of transparent exopolymeric particles (TEP) to estuarine particulate organic carbon pool, Mar. Ecol. Prog. Ser., 529, 17–34, https://doi.org/10.3354/meps11294, 2015.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

Arnosti, C., Wietz, M., Brinkhoff, T., Hehemann, J.-H., Probandt, D., Zeugner, L., and Amann, R.: The Biogeochemistry of Marine Polysaccharides: Sources, Inventories, and Bacterial Drivers of the Carbohydrate Cycle, Annu. Rev. Mar. Sci., 13, 81–108, https://doi.org/10.1146/annurev-marine-032020-012810, 2021.

Ascani, F., Richards, K. J., Firing, E., Grant, S., Johnson, K. S., Jia, Y., Lukas, R., and Karl, D. M.: Physical and biological controls of nitrate concentrations in the upper subtropical North Pacific Ocean, Deep Sea Res. Part II Top. Stud. Oceanogr., 93, 119–134, https://doi.org/10.1016/j.dsr2.2013.01.034, 2013.

Azetsu-Scott, K. and Passow, U.: Ascending marine particles: Significance of transparent exopolymer particles (TEP) in the upper ocean, Limnol. Oceanogr., 49, 741–748, https://doi.org/10.4319/lo.2004.49.3.0741, 2004.

Bar-Zeev, E., Berman, T., Rahav, E., Dishon, G., Herut, B., Kress, N., and Berman-Frank, I.: Transparent exopolymer particle (TEP) dynamics in the eastern Mediterranean Sea, Mar. Ecol. Prog. Ser., 431, 107–118, https://doi.org/10.3354/meps09110, 2011.

Beauvais, S., Pedrotti, M. L., Villa, E., and Lemée, R.: Transparent exopolymer particle (TEP) dynamics in relation to trophic and hydrological conditions in the NW Mediterranean Sea, Mar. Ecol. Prog. Ser., 262, 97–109, https://doi.org/10.3354/meps262097, 2003.

Berman-Frank, I., Rosenberg, G., Levitan, O., Haramaty, L., and Mari, X.: Coupling between autocatalytic cell death and transparent exopolymeric particle production in the marine cyanobacterium Trichodesmium, Environ. Microbiol., 9, 1415–1422, https://doi.org/10.1111/j.1462-2920.2007.01257.x, 2007.

Bhosle, N. B., Bhaskar, P. V., and Ramachandran, S.: Abundance of dissolved polysaccharides in the oxygen minimum layer of the Northern Indian Ocean, Mar. Chem., 63, 171–182, https://doi.org/10.1016/S0304-4203(98)00061-9, 1998.

Böttjer, D., Dore, J. E., Karl, D. M., Letelier, R. M., Mahaffey, C., Wilson, S. T., Zehr, J., and Church, M. J.: Temporal variability of nitrogen fixation and particulate nitrogen export at Station ALOHA, Limnol. Oceanogr., 62, 200–216, https://doi.org/10.1002/lno.10386, 2017.

Buesseler, K. O., Antia, A. N., Chen, M., Fowler, S. W., Gardner, W. D., Gustafsson, O., Harada, K., Michaels, A. F., Rutgers van der Loeff, M., Sarin, M., Steinberg, D. K., and Trull, T.: An assessment of the use of sediment traps for estimating upper ocean particle fluxes, J. Mar. Res., 65, 345–416, https://doi.org/10.1357/002224007781567621, 2007.

Burney, C. M., Johnson, K. M., Lavoie, D. M., and Sieburth, J. McN.: Dissolved carbohydrate and microbial ATP in the North Atlantic: concentrations and interactions, Deep Sea Res. Part Oceanogr. Res. Pap., 26, 1267–1290, https://doi.org/10.1016/0198-0149(79)90068-2, 1979.

Busch, K., Endres, S., Iversen, M. H., Michels, J., Nöthig, E.-M., and Engel, A.: Bacterial Colonization and Vertical Distribution of Marine Gel Particles (TEP and CSP) in the Arctic Fram Strait, Front. Mar. Sci., 4, 2017.

Chin, W.-C., Orellana, M. V., and Verdugo, P.: Spontaneous assembly of marine dissolved organic matter into polymer gels, Nature, 391, 568–572, https://doi.org/10.1038/35345, 1998.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

Chow, C. H., Cheah, W., and Tai, J.-H.: A rare and extensive summer bloom enhanced by ocean eddies in the oligotrophic western North Pacific Subtropical Gyre, Sci. Rep., 7, 6199, https://doi.org/10.1038/s41598-017-06584-3, 2017.

Cisternas-Novoa, C., Lee, C., and Engel, A.: Transparent exopolymer particles (TEP) and Coomassie stainable particles (CSP): Differences between their origin and vertical distributions in the ocean, Mar. Chem., 175, 56–71, https://doi.org/10.1016/j.marchem.2015.03.009, 2015.

Dave, A. C. and Lozier, M. S.: Local stratification control of marine productivity in the subtropical North Pacific, J. Geophys. Res. Oceans, 115, https://doi.org/10.1029/2010JC006507, 2010.

Emerson, S.: Annual net community production and the biological carbon flux in the ocean, Glob. Biogeochem. Cycles, 28, 14–28, https://doi.org/10.1002/2013GB004680, 2014.

Emerson, S. and Hayward, T.: Chemical tracers of biological processes in shallow waters of North Pacific: preformed nitrate distributions., J. Mar. Res., 53, 499–513, 1995.

Emerson, S., Quay, P., Karl, D., Winn, C., Tupas, L., and Landry, M.: Experimental determination of the organic carbon flux from open-ocean surface waters, Nature, 389, 951–954, https://doi.org/10.1038/40111, 1997.

Engel, A. and Passow, U.: Carbon and nitrogen content of transparent exopolymer particles (TEP) in relation to their Alcian Blue adsorption, Mar. Ecol. Prog. Ser., 219, 1–10, https://doi.org/10.3354/meps219001, 2001.

Engel, A., Borchard, C., Loginova, A., Meyer, J., Hauss, H., and Kiko, R.: Effects of varied nitrate and phosphate supply on polysaccharidic and proteinaceous gel particle production during tropical phytoplankton bloom experiments, Biogeosciences, 12, 5647–5665, https://doi.org/10.5194/bg-12-5647-2015, 2015.

Engel, A., Endres, S., Galgani, L., and Schartau, M.: Marvelous Marine Microgels: On the Distribution and Impact of Gel-Like Particles in the Oceanic Water-Column, Front. Mar. Sci., 7, https://doi.org/10.3389/fmars.2020.00405, 2020.

Fawcett, S. E., Johnson, K. S., Riser, S. C., Van Oostende, N., and Sigman, D. M.: Low-nutrient organic matter in the Sargasso Sea thermocline: A hypothesis for its role, identity, and carbon cycle implications, Mar. Chem., 207, 108–123, https://doi.org/10.1016/j.marchem.2018.10.008, 2018.

Goldberg, S. J., Carlson, C. A., Bock, B., Nelson, N. B., and Siegel, D. A.: Meridional variability in dissolved organic matter stocks and diagenetic state within the euphotic and mesopelagic zone of the North Atlantic subtropical gyre, Mar. Chem., 119, 9–21, https://doi.org/10.1016/j.marchem.2009.12.002, 2010.

Grossart, H.-P., Czub, G., and Simon, M.: Algae–bacteria interactions and their effects on aggregation and organic matter flux in the sea, Environ. Microbiol., 8, 1074–1084, https://doi.org/10.1111/j.1462-2920.2006.00999.x, 2006.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

Gruber, N., Keeling, C. D., and Stocker, T. F.: Carbon-13 constraints on the seasonal inorganic carbon budget at the BATS site in the northwestern Sargasso Sea, Deep Sea Res. Part Oceanogr. Res. Pap., 45, 673–717, https://doi.org/10.1016/S0967-0637(97)00098-8, 1998.

Guo, S., Wu, Y., Zhu, M., and Sun, X.: Concentrations of transparent exopolymer particles (TEPs) and their role in the carbon export in the South China Sea and western tropical North Pacific, Mar. Environ. Res., 179, 105699, https://doi.org/10.1016/j.marenvres.2022.105699, 2022.

Hannides, C. C. S., Popp, B. N., Landry, M. R., and Graham, B. S.: Quantification of zooplankton trophic position in the North Pacific Subtropical Gyre using stable nitrogen isotopes, Limnol. Oceanogr., 54, 50–61, https://doi.org/10.4319/lo.2009.54.1.0050, 2009.

Iuculano, F., Mazuecos, I. P., Reche, I., and Agustí, S.: Prochlorococcus as a Possible Source for Transparent Exopolymer Particles (TEP), Front. Microbiol., 8, 2017.

von Jackowski, A., Grosse, J., Nöthig, E.-M., and Engel, A.: Dynamics of organic matter and bacterial activity in the Fram Strait during summer and autumn, Philos. Trans. R. Soc. Math. Phys. Eng. Sci., 378, 20190366, https://doi.org/10.1098/rsta.2019.0366, 2020.

Johnson, K. S., Riser, S. C., and Karl, D. M.: Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre, Nature, 465, 1062–1065, https://doi.org/10.1038/nature09170, 2010.

Kaiser, K. and Benner, R.: Organic matter transformations in the upper mesopelagic zone of the North Pacific: Chemical composition and linkages to microbial community structure, J. Geophys. Res. Oceans, 117, https://doi.org/10.1029/2011JC007141, 2012.

Karl, D. M., Church, M. J., Dore, J. E., Letelier, R. M., and Mahaffey, C.: Predictable and efficient carbon sequestration in the North Pacific Ocean supported by symbiotic nitrogen fixation, Proc. Natl. Acad. Sci., 109, 1842–1849, https://doi.org/10.1073/pnas.1120312109, 2012.

Karl, D. M., Letelier, R. M., Bidigare, R. R., Björkman, K. M., Church, M. J., Dore, J. E., and White, A. E.: Seasonal-to-decadal scale variability in primary production and particulate matter export at Station ALOHA, Prog. Oceanogr., 195, 102563, https://doi.org/10.1016/j.pocean.2021.102563, 2021.

Keeling, C. D., Brix, H., and Gruber, N.: Seasonal and long-term dynamics of the upper ocean carbon cycle at Station ALOHA near Hawaii, Glob. Biogeochem. Cycles, 18, https://doi.org/10.1029/2004GB002227, 2004.

Lamborg, C. H., Buesseler, K. O., Valdes, J., Bertrand, C. H., Bidigare, R., Manganini, S., Pike, S., Steinberg, D., Trull, T., and Wilson, S.: The flux of bio- and lithogenic material associated with sinking particles in the mesopelagic “twilight zone” of the northwest and North Central Pacific Ocean, Deep Sea Res. Part II Top. Stud. Oceanogr., 55, 1540–1563, https://doi.org/10.1016/j.dsr2.2008.04.011, 2008.

Letelier, R. M., Björkman, K. M., Church, M. J., Hamilton, D. S., Mahowald, N. M., Scanza, R. A., Schneider, N., White, A. E., and Karl, D. M.: Climate-driven oscillation of phosphorus and iron limitation in the North Pacific Subtropical Gyre, Proc. Natl. Acad. Sci., 116, 12720–12728, https://doi.org/10.1073/pnas.1900789116, 2019.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

Letscher, R. T. and Villareal, T. A.: Evaluation of the seasonal formation of subsurface negative preformed nitrate anomalies in the subtropical North Pacific and North Atlantic, Biogeosciences, 15, 6461–6480, https://doi.org/10.5194/bg-15-6461-2018, 2018.

Liang, Z., Letscher, R. T., and Knapp, A. N.: Global patterns of surface ocean dissolved organic matter stoichiometry, *Global Biogeochemical Cycles*, *37*(12), e2023GB007788, https://doi.org/10.1029/2023GB007788, 2023.

Ling, S. C. and Alldredge, A. L.: Does the marine copepod Calanus pacificus consume transparent exopolymer particles (TEP)?, J. Plankton Res., 25, 507–515, https://doi.org/10.1093/plankt/25.5.507, 2003.

Long, J., Fassbender, A., and Estapa, M.: Depth-Resolved Net Primary Production in the Northeast Pacific Ocean: A Comparison of Satellite and Profiling Float Estimates in the Context of Two Marine Heatwaves, Geophys. Res. Lett., 48, https://doi.org/10.1029/2021GL093462, 2021.

Longhurst, A., Sathyendranath, S., Platt, T., and Caverhill, C.: An estimate of global primary production in the ocean from satellite radiometer data, J. Plankton Res., 17, 1245–1271, https://doi.org/10.1093/plankt/17.6.1245, 1995.

Mari, X., Beauvais, S., Lemée, R., and Pedrotti, M. L.: Non-Redfield C:N ratio of transparent exopolymeric particles in the northwestern Mediterranean Sea, Limnol. Oceanogr., 46, 1831–1836, https://doi.org/10.4319/lo.2001.46.7.1831, 2001.

Mari, X., Rochelle-Newall, E., Torréton, J.-P., Pringault, O., Jouon, A., and Migon, C.: Water residence time: A regulatory factor of the DOM to POM transfer efficiency, Limnol. Oceanogr., 52, 808–819, https://doi.org/10.4319/lo.2007.52.2.0808, 2007.

Mari, X., Passow, U., Migon, C., Burd, A. B., and Legendre, L.: Transparent exopolymer particles: Effects on carbon cycling in the ocean, Prog. Oceanogr., 151, 13–37, https://doi.org/10.1016/j.pocean.2016.11.002, 2017.

McCarthy, M., Hedges, J., and Benner, R.: Major biochemical composition of dissolved high molecular weight organic matter in seawater, Mar. Chem., 55, 281–297, https://doi.org/10.1016/S0304-4203(96)00041-2, 1996.

Meers, E., Laing, G. D., Unamuno, V. G., Lesage, E., Tack, F. M. G., and Verloo, M. G.: Water Extractability of Trace Metals from Soils: Some Pitfalls, Water. Air. Soil Pollut., 176, 21–35, https://doi.org/10.1007/s11270-005-9070-1, 2006.

Michaels, A. F., Bates, N. R., Buesseler, K. O., Carlson, C. A., and Knap, A. H.: Carbon-cycle imbalances in the Sargasso Sea, Nature, 372, 537–540, https://doi.org/10.1038/372537a0, 1994.

Nagata, T., Yamada, Y., and Fukuda, H.: Transparent Exopolymer Particles in Deep Oceans: Synthesis and Future Challenges, Gels, 7, 75, https://doi.org/10.3390/gels7030075, 2021.

Nosaka, Y., Yamashita, Y., and Suzuki, K.: Dynamics and Origin of Transparent Exopolymer Particles in the Oyashio Region of the Western Subarctic Pacific during the Spring Diatom Bloom, Front. Mar. Sci., 4, 2017.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

Ortega-Retuerta, E., Passow, U., Duarte, C. M., and Reche, I.: Effects of ultraviolet B radiation on (not so) transparent exopolymer particles, Biogeosciences, 6, 3071–3080, https://doi.org/10.5194/bg-6-3071-2009, 2009a.

Ortega-Retuerta, E., Reche, I., Pulido-Villena, E., Agustí, S., and Duarte, C. M.: Uncoupled distributions of transparent exopolymer particles (TEP) and dissolved carbohydrates in the Southern Ocean, Mar. Chem., 115, 59–65, https://doi.org/10.1016/j.marchem.2009.06.004, 2009b.

Ortega-Retuerta, E., Mazuecos, I. P., Reche, I., Gasol, J. M., Álvarez-Salgado, X. A., Álvarez, M., Montero, M. F., and Arístegui, J.: Transparent exopolymer particle (TEP) distribution and in situ prokaryotic generation across the deep Mediterranean Sea and nearby North East Atlantic Ocean, Prog. Oceanogr., 173, 180–191, https://doi.org/10.1016/j.pocean.2019.03.002, 2019.

Pakulski, J. D. and Benner, R.: Abundance and distribution of carbohydrates in the ocean, Limnol. Oceanogr., 39, 930–940, https://doi.org/10.4319/lo.1994.39.4.0930, 1994.

Passow, U.: Formation of transparent exopolymer particles, TEP, from dissolved precursor material, Mar. Ecol. Prog. Ser., 192, 1–11, https://doi.org/10.3354/meps192001, 2000.

Passow, U.: Production of transparent exopolymer particles (TEP) by phyto- and bacterioplankton, Mar. Ecol. Prog. Ser., 236, 1–12, https://doi.org/10.3354/meps236001, 2002a.

Passow, U.: Transparent exopolymer particles (TEP) in aquatic environments, Prog. Oceanogr., 55, 287–333, https://doi.org/10.1016/S0079-6611(02)00138-6, 2002b.

Passow, U., Alldredge, A. L., and Logan, B. E.: The role of particulate carbohydrate exudates in the flocculation of diatom blooms, Deep Sea Res. Part Oceanogr. Res. Pap., 41, 335–357, https://doi.org/10.1016/0967-0637(94)90007-8, 1994.

Pilskaln, C. H., Villareal, T. A., Dennett, M., Darkangelo-Wood, C., and Meadows, G.: High concentrations of marine snow and diatom algal mats in the North Pacific Subtropical Gyre: Implications for carbon and nitrogen cycles in the oligotrophic ocean, Deep Sea Res. Part Oceanogr. Res. Pap., 52, 2315–2332, https://doi.org/10.1016/j.dsr.2005.08.004, 2005.

van Pinxteren, M., Robinson, T.-B., Zeppenfeld, S., Gong, X., Bahlmann, E., Fomba, K. W., Triesch, N., Stratmann, F., Wurl, O., Engel, A., Wex, H., and Herrmann, H.: High number concentrations of transparent exopolymer particles in ambient aerosol particles and cloud water – a case study at the tropical Atlantic Ocean, Atmospheric Chem. Phys., 22, 5725–5742, https://doi.org/10.5194/acp-22-5725-2022, 2022.

Prairie, J. C., Montgomery, Q. W., Proctor, K. W., and Ghiorso, K. S.: Effects of Phytoplankton Growth Phase on Settling Properties of Marine Aggregates, J. Mar. Sci. Eng., 7, 265, https://doi.org/10.3390/jmse7080265, 2019.

Quay, P., Emerson, S., and Palevsky, H.: Regional Pattern of the Ocean's Biological Pump Based on Geochemical Observations, Geophys. Res. Lett., 47, e2020GL088098, https://doi.org/10.1029/2020GL088098, 2020.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

Rabouille, S., Cabral, G. S., and Pedrotti, M. L.: Towards a carbon budget of the diazotrophic cyanobacterium Crocosphaera: effect of irradiance, Mar. Ecol. Prog. Ser., 570, 29–40, https://doi.org/10.3354/meps12087, 2017.

Radić, T., Ivančić, I., Fuks, D., and Radić, J.: Marine bacterioplankton production of polysaccharidic and proteinaceous particles under different nutrient regimes, FEMS Microbiol. Ecol., 58, 333–342, https://doi.org/10.1111/j.1574-6941.2006.00176.x, 2006.

Reintjes, G., Fuchs, B. M., Amann, R., and Arnosti, C.: Extensive Microbial Processing of Polysaccharides in the South Pacific Gyre via Selfish Uptake and Extracellular Hydrolysis, Front. Microbiol., 11, 2020.

Reygondeau, G., Longhurst, A., Martinez, E., Beaugrand, G., Antoine, D., and Maury, O.: Dynamic biogeochemical provinces in the global ocean, Glob. Biogeochem. Cycles, 27, 1046–1058, https://doi.org/10.1002/gbc.20089, 2013.

Rochelle-Newall, E. J., Mari, X., and Pringault, O.: Sticking properties of transparent exopolymeric particles (TEP) during aging and biodegradation, J. Plankton Res., 32, 1433–1442, https://doi.org/10.1093/plankt/fbq060, 2010.

Roshan, S. and DeVries, T.: Efficient dissolved organic carbon production and export in the oligotrophic ocean, Nat. Commun., 8, 2036, https://doi.org/10.1038/s41467-017-02227-3, 2017.

Sambrotto, R. N., Savidge, G., Robinson, C., Boyd, P., Takahashi, T., Karl, D. M., Langdon, C., Chipman, D., Marra, J., and Codispoti, L.: Elevated consumption of carbon relative to nitrogen in the surface ocean, Nature, 363, 248–250, https://doi.org/10.1038/363248a0, 1993.

Smith, D. C., Simon, M., Alldredge, A. L., and Azam, F.: Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution, Nature, 359, 139–142, https://doi.org/10.1038/359139a0, 1992.

Smyth, A. J., and Letscher, R. T.: Spatial and temporal occurrence of preformed nitrate anomalies in the subtropical North Pacific and North Atlantic oceans, *Marine Chemistry*, *252*, 104248, https://doi.org/10.5194/bg-15-6461-2018, 2023.

Sun, C.-C., Sperling, M., and Engel, A.: Effect of wind speed on the size distribution of gel particles in the sea surface microlayer: insights from a wind–wave channel experiment, Biogeosciences, 15, 3577–3589, https://doi.org/10.5194/bg-15-3577-2018, 2018.

Teng, Y.-C., Primeau, F. W., Moore, J. K., Lomas, M. W., and Martiny, A. C.: Global-scale variations of the ratios of carbon to phosphorus in exported marine organic matter, Nat. Geosci., 7, 895–898, https://doi.org/10.1038/ngeo2303, 2014.

Thompson, A. W., van den Engh, G., Ahlgren, N. A., Kouba, K., Ward, S., Wilson, S. T., and Karl, D. M.: Dynamics of Prochlorococcus Diversity and Photoacclimation During Short-Term Shifts in Water Column Stratification at Station ALOHA, Front. Mar. Sci., 5, 2018.

Thornton, D. C. O.: Coomassie Stainable Particles (CSP): Protein Containing Exopolymer Particles in the Ocean, Front. Mar. Sci., 5, 2018.

https://doi.org/10.5194/egusphere-2024-1416
Preprint. Discussion started: 12 June 2024

877 Toggweiler, J. R.: Carbon overconsumption, Nature, 363, 210–211, https://doi.org/10.1038/363210a0,
878 1993.

879 Villareal, T. A., Pilskaln, C. H., Montoya, J. P., and Dennett, M.: Upward nitrate transport by
880 phytoplankton in oceanic waters: balancing nutrient budgets in oligotrophic seas, PeerJ, 2, e302,
881 https://doi.org/10.7717/peerj.302, 2014.

882 Westberry, T. K., Silsbe, G. M., and Behrenfeld, M. J.: Gross and net primary production in the global
883 ocean: An ocean color remote sensing perspective, Earth-Sci. Rev., 237, 104322,
884 https://doi.org/10.1016/j.earscirev.2023.104322, 2023.

885 Williams, P. J. le B., Quay, P. D., Westberry, T. K., and Behrenfeld, M. J.: The Oligotrophic Ocean Is
886 Autotrophic, Annu. Rev. Mar. Sci., 5, 535–549, https://doi.org/10.1146/annurev-marine-121211-172335,
887 2013.

888 Wurl, O., Wurl, E., Miller, L., Johnson, K., and Vagle, S.: Formation and global distribution of sea-surface
889 microlayers, Biogeosciences, 8, 121–135, https://doi.org/10.5194/bg-8-121-2011, 2011a.

890 Wurl, O., Miller, L., and Vagle, S.: Production and fate of transparent exopolymer particles in the ocean,
891 J. Geophys. Res. Oceans, 116, https://doi.org/10.1029/2011JC007342, 2011b.

892 Zamanillo, M., Ortega-Retuerta, E., Nunes, S., Estrada, M., Sala, M. M., Royer, S.-J., López-Sandoval, D.
893 C., Emelianov, M., Vaqué, D., Marrasé, C., and Simó, R.: Distribution of transparent exopolymer particles
894 (TEP) in distinct regions of the Southern Ocean, Sci. Total Environ., 691, 736–748,
895 https://doi.org/10.1016/j.scitotenv.2019.06.524, 2019.

896 Zamanillo, M., Ortega-Retuerta, E., Cisternas-Novoa, C., Marrasé, C., Pelejero, C., Pascual, J., Gasol, J. M.,
897 Engel, A., and Simó, R.: Uncoupled seasonal variability of transparent exopolymer and Coomassie
898 stainable particles in coastal Mediterranean waters: Insights into sources and driving mechanisms, Elem.
899 Sci. Anthr., 9, 00165, https://doi.org/10.1525/elementa.2020.00165, 2021.

900 Zäncker, B., Bracher, A., Röttgers, R., and Engel, A.: Variations of the Organic Matter Composition in the
901 Sea Surface Microlayer: A Comparison between Open Ocean, Coastal, and Upwelling Sites Off the
902 Peruvian Coast, Front. Microbiol., 8, 2017.

903

904